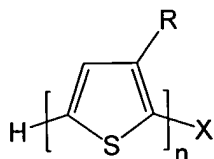


THEREFORE, WE CLAIM:

1. A polythiophene polymer, the polymer having the structure:



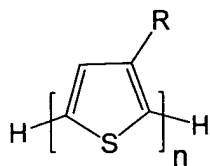
wherein R is a substituent selected from the group consisting of alkyl, polyether, and aryl, X is a halogen, and n is greater than 1,

the polymer being formed from a polymerization reaction in major amounts of at least 90% by weight.

2. The polythiophene polymer of claim 1, wherein R is an alkyl group.
3. The polythiophene polymer of claim 1, wherein R is an alkyl group having from 1 to 15 carbon atoms.
4. The polythiophene polymer of claim 1, wherein R is an alkyl group having from 4 to 15 carbon atoms.
5. The polythiophene polymer of claim 1, wherein R is an alkyl group having from 4 to 12 carbon atoms.
6. The polythiophene polymer of claim 1, wherein R is an alkyl group selected from the group consisting of butyl, hexyl, octyl, and dodecyl.
7. The polythiophene polymer of claim 1, wherein X is a halogen selected from the group consisting of Cl, Br, and I.
8. The polythiophene polymer of claim 1, wherein X is Br.

9. The polythiophene polymer of claim 1, wherein the polymer is formed from the polymerization reaction in major amounts of at least 95% by weight.

10. A polythiophene polymer, the polymer having the structure:



wherein R is a substituent selected from the group consisting of alkyl, polyether, and aryl, and n is greater than 1,

the polymer being formed from a polymerization reaction in major amounts of at least 90% by weight.

11. The polythiophene polymer of claim 10, wherein R is an alkyl group.

12. The polythiophene polymer of claim 10, wherein R is an alkyl group having 1 to 15 carbon atoms.

13. The polythiophene polymer of claim 10, wherein R is an alkyl group having 4 to 15 carbon atoms.

14. The polythiophene polymer of claim 10, wherein R is an alkyl group having 4 to 12 carbon atoms.

15. The polythiophene polymer of claim 10, wherein R is an alkyl group selected from the group consisting of butyl, hexyl, octyl, and dodecyl.

16. The polythiophene polymer of claim 10, wherein the polymer is formed from the polymerization reaction in major amounts of at least 95% by weight.

17. The polythiophene polymer of claim 10, wherein the polymer is formed from the polymerization reaction in major amounts of at least 99% by weight.

18. The polythiophene polymer of claim 10, wherein essentially all of a product from the polymerization reaction is the polymer.

10  
19. A method of forming a polymer, comprising:  
combining a soluble thiophene monomer with an amide base and a divalent metal halide; and  
adding an effective amount of a Ni(II) catalyst to initiate a polymerization reaction to form at least 90% by weight of the polymer having the structure



wherein R is a substituent selected from the group consisting of alkyl, polyether, and aryl, X is a halogen, and n is greater than 1.

11  
20. The method of claim 10, wherein the amide base is lithium diisopropylamide.

12  
21. The method of claim 20, wherein the lithium diisopropylamide and divalent metal halide are added to the thiophene monomer at a temperature ranging from -78°C to -60°C.

13  
22. The method of claim 10, wherein the divalent metal halide is zinc chloride.

14  
23. The method of claim 10, wherein the Ni(II) catalyst is selected from the group consisting of 1,3-diphenylphosphinopropane nickel(II) chloride and 1,2-bis(diphenylphosphino)ethane nickel(II) chloride.

15  
24. The method of claim 10, wherein R is an alkyl group.

16  
25. The method of claim 10, wherein R is an alkyl group having 1 to 15 carbon atoms.

17  
26. The method of claim 10, wherein R is an alkyl group having 4 to 15 carbon atoms.

18  
27. The method of claim 10, wherein R is an alkyl group having 4 to 12 carbon atoms.

19  
28. The method of claim 10, wherein R is an alkyl group selected from the group consisting of butyl, hexyl, octyl, and dodecyl.

20  
29. The method of claim 10, wherein X is a halogen selected from the group consisting of Cl, Br, and I.

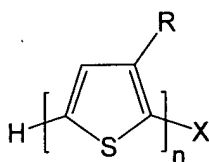
21  
30. The method of claim 20, wherein X is Br.

22  
31. The method of claim 10, further comprising quenching the reaction to form the polymer.

23  
32. The method of claim 10, wherein the polymer is formed from the polymerization reaction in major amounts of at least 95% by weight.

24  
33. A method of forming a polymer, comprising:  
combining a soluble thiophene monomer with an amide base and zinc chloride at a temperature ranging from -78°C to -60°C; and  
adding an effective amount of a Ni(II) catalyst to initiate a polymerization reaction.

25  
34. The method of claim 33, wherein the polymer has the structure:



wherein R is a substituent selected from the group consisting of alkyl, polyether, and aryl, X is a halogen, and n is greater than 1.

<sup>26</sup>  
~~35.~~ The method of claim ~~34~~<sup>25</sup>, wherein the polymer is at least 90% by weight of a reaction product of the reaction.

<sup>27</sup>  
~~36.~~ The method of claim ~~34~~<sup>25</sup>, wherein R is an alkyl group.

<sup>28</sup>  
~~37.~~ The method of claim ~~34~~<sup>25</sup>, wherein R is an alkyl group having 1 to 15 carbon atoms.

<sup>29</sup>  
~~38.~~ The method of claim ~~34~~<sup>25</sup>, wherein R is an alkyl group having 4 to 15 carbon atoms.

<sup>30</sup>  
~~39.~~ The method of claim ~~34~~<sup>25</sup>, wherein R is an alkyl group having 4 to 12 carbon atoms.

<sup>31</sup>  
~~40.~~ The method of claim ~~34~~<sup>25</sup>, wherein R is an alkyl group selected from the group consisting of butyl, hexyl, octyl, and dodecyl.

<sup>32</sup>  
~~41.~~ The method of claim ~~34~~<sup>25</sup>, wherein X is a halogen selected from the group consisting of Cl, Br, and I.

<sup>33</sup>  
~~42.~~ The method of claim ~~41~~<sup>32</sup>, wherein X is Br.

<sup>34</sup>  
~~43.~~ The method of claim ~~33~~<sup>24</sup>, wherein the polymer is formed from the polymerization reaction in major amounts of at least 95% by weight.

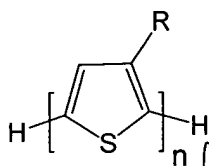
<sup>35</sup>  
~~44.~~ The method of claim ~~33~~<sup>24</sup>, wherein the amide base is lithium diisopropylamide.

36  
45. The method of claim 33, wherein the Ni(II) catalyst is selected from the group consisting of 1,3-diphenylphosphinopropane nickel(II) chloride and 1,2-bis(diphenylphosphino)ethane nickel(II) chloride.

41  
46. The method of claim 33, further comprising quenching the reaction to form the polymer.

47. A method of forming a polymer, comprising:

combining a soluble thiophene with an organomagnesium reagent, wherein the organomagnesium reagent has the formula  $R'MgX'$  and  $R'$  is a substituent selected from the group consisting of alkyl, vinyl and phenyl and  $X'$  is a halogen, to form at least 90% by weight of a polythiophene polymer having the structure:



wherein  $R$  is a substituent selected from the group consisting of alkyl, polyether, and aryl, and  $n$  is greater than 1.

48. The method of claim 47, further comprising adding an amount of tetrahydrofuran with the organomagnesium reagent.

49. The method of claim 47 wherein  $X'$  is a halogen selected from the group consisting of Br and I.

50. The method of claim 47 wherein  $R$  is an alkyl group.

51. The method of claim 47, wherein the organomagnesium reagent is *tert*-butylMgBr.

52. The method of claim 47 wherein said Ni(II) catalyst is one of 1,3-diphenylphosphinopropane nickel(II) chloride and 1,2-bis(diphenylphosphino)ethane nickel(II) chloride.

53. The method of claim 47 wherein R and R' are each an alkyl group.

54. The method of claim 47, wherein R is an alkyl group having 1 to 15 carbon atoms.

55. The method of claim 47, wherein R is an alkyl group having 4 to 15 carbon atoms.

56. The method of claim 47, wherein R is an alkyl group having 4 to 12 carbon atoms.

57. The method of claim 47, wherein the polymer is formed from the polymerization reaction in major amounts of at least 95% by weight.

58. The method of claim 47, wherein the polymer is formed from the polymerization reaction in major amounts of at least 99% by weight.

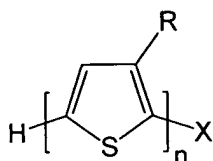
59. The method of claim 47, wherein essentially all of a product from the polymerization reaction is the polymer.

38  
60.

A method of forming a polymer, comprising:

combining a soluble thiophene monomer with an amide base and a divalent metal halide;

adding an effective amount of a first Ni(II) catalyst to initiate a polymerization reaction to form at least 90% by weight of an intermediate polymer having the structure:



wherein R is a substituent selected from the group consisting of alkyl, polyether, and aryl, X is a halogen, and n is greater than 1;

adding a derivative compound represented by the formula PFG-A-MX' and a second Ni(II) catalyst to the intermediate polymer to form a protected thiophene polymer, wherein PFG is a protected hydroxyl or amine functional group, A is selected from the group consisting of alkyl and aromatic, M is selected from the group consisting of Zn <sup>and</sup> Mg, and X' is a halogen; and

deprotecting the protected thiophene polymer in an acid environment to form the deprotected polymer having one functional end group.

39 38  
61. The method of claim 60, wherein the amide base is lithium diisopropylamide.

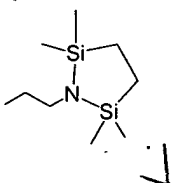
40 39  
62. The method of claim 61, wherein the lithium diisopropylamide and divalent metal halide are added to the thiophene monomer at a temperature ranging from -78°C to -60°C.

41 38  
63. The method of claim 60, wherein the divalent metal halide is zinc chloride.

42 38  
64. The method of claim 60, wherein the first and the second Ni(II) catalyst are selected from the group consisting of 1,3-diphenylphosphinopropane nickel(II) chloride and 1,2-bis(diphenylphosphino)ethane nickel(II) chloride.

43 38  
65. The method of claim 60, wherein A is selected from the group consisting of benzene and thiophene, X' is selected from the group consisting of Br and Cl, and PFG is selected from the group consisting of -CH<sub>2</sub>CH<sub>2</sub>O(tetrahydropyran),

72470  
-CH<sub>2</sub>CH<sub>2</sub>O(trimethylsilane), and





44

58

66. The method of claim 60, wherein deprotecting the protected thiophene polymer comprises adding acid agents with a refluxing solvent.

45

44

67. The method of claim 66, wherein the acid agents include hydrochloric acid, and the refluxing solvent is tetrahydrofuran.

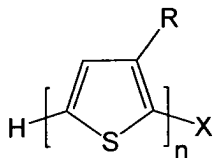
46

68. A method of forming a polymer, comprising:  
 combining a soluble thiophene monomer with an amide base and zinc chloride at a temperature ranging from  $-78^{\circ}\text{C}$  to  $-60^{\circ}\text{C}$ ;  
 adding an effective amount of a first Ni(II) catalyst to initiate a polymerization reaction and form an intermediate polymer;  
 adding a derivative compound represented by the formula PFG-A-MX' and a second Ni(II) catalyst to the intermediate polymer to form a protected thiophene polymer, wherein PFG is a protected hydroxyl or amine functional group, A is selected from the group consisting of alkyl and aromatic, M is a selected from the group consisting of Zn, <sup>and</sup> Mg, and X' is a halogen; and  
 deprotecting the protected thiophene polymer in an acid environment to form the deprotected polymer having one functional end group.

47

41

69. The method of claim 68, wherein the intermediate polymer has the structure:



wherein R is a substituent selected from the group consisting of alkyl, polyether, and aryl, X is a halogen, and n is greater than 1.

48

46

70. The method of claim 68, wherein the amide base is lithium diisopropylamide.

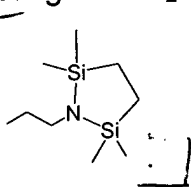
71. The method of claim 70, wherein the lithium diisopropylamide and divalent metal halide are added to the thiophene monomer at a temperature ranging from  $-78^{\circ}\text{C}$  to

49  
-60°C

46  
72. The method of claim 68, wherein the first and the second Ni(II) catalyst are selected from the group consisting of 1,3-diphenylphosphinopropane nickel(II) chloride and 1,2-bis(diphenylphosphino)ethane nickel(II) chloride.

50  
46  
73. The method of claim 68, wherein A is selected from the group consisting of benzene and thiophene, X' is selected from the group consisting of Br and Cl, and PFG is selected from the group consisting of -CH<sub>2</sub>CH<sub>2</sub>O(tetrahydropyran),

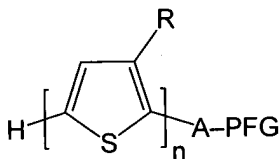
7090  
-CH<sub>2</sub>CH<sub>2</sub>O(trimethylsilane), and



51  
46  
74. The method of claim 68, wherein deprotecting the protected thiophene polymer comprises adding acid agents with a refluxing solvent.

52  
51  
75. The method of claim 74, wherein the acid agents include hydrochloric acid, and the refluxing solvent is tetrahydrofuran.

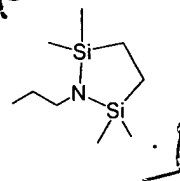
53  
76. A protected thiophene polymer having the structure:



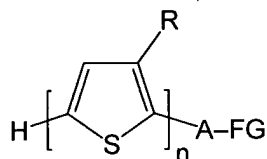
7091  
wherein PFG is a protected hydroxyl or amine functional group, and A is selected from the group consisting of alkyl and aromatic, the protected thiophene polymer formed from the polymer of claim 1.

54  
77. The protected thiophene polymer of claim 76, wherein A is selected from the group consisting of benzene and thiophene, and PFG is selected from the group

consisting of  $-\text{CH}_2\text{CH}_2\text{O}(\text{tetrahydropyran})$ ,  $-\text{CH}_2\text{CH}_2\text{O}(\text{trimethylsilane})$ , and



55  
78. A deprotected polymer having one functional end group having the structure:



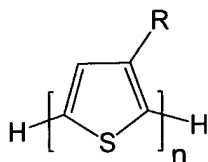
wherein R is selected from the group consisting of alkyl, polyether, and aryl; n is greater than 1; A is selected from the group consisting of alkyl and aromatic, and FG is a functional group selected from the group consisting of primary alkyl amine and primary alcohol,

the deprotected polymer formed from the polymer of claim 1.

56  
79. The deprotected polymer of claim 78, wherein A is selected from the group consisting of benzene and thiophene; and FG is a functional group selected from the group consisting of carboxylic acid,  $-\text{CH}_2\text{CH}_2\text{OH}$ , and  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ .

57  
80. A method of forming a poly-(3-substituted) thiophene diol, comprising:

combining a soluble thiophene with an organomagnesium reagent, wherein the organomagnesium reagent has the formula  $\text{R}'\text{MgX}'$  and  $\text{R}'$  is a substituent selected from the group consisting of alkyl, vinyl and phenyl and  $\text{X}'$  is a halogen, to form at least 90% by weight of a polythiophene intermediate polymer having the structure:



wherein R is a substituent selected from the group consisting of alkyl, polyether, and aryl, and n is greater than 1;

introducing aldehyde groups to both ends of a chain of the intermediate polymer;  
and  
reducing the aldehyde groups to yield the poly-(3-substituted) thiophene diol.

58 57  
81. The method of claim 80, further comprising adding an amount of tetrahydrofuran with the organomagnesium reagent.

59 57  
82. The method of claim 80 wherein X' is a halogen selected from the group consisting of Br and I.

60 57  
83. The method of claim 80 wherein R' is an alkyl group.

61 57  
84. The method of claim 80 wherein the Ni(II) catalyst is one of 1,3-diphenylphosphinopropane nickel(II) chloride and 1,2-bis(diphenylphosphino)ethane nickel(II) chloride.

62 57  
85. The method of claim 80, wherein R and R' are an alkyl group.

63 57  
86. The method of claim 80, wherein the polymer is formed from the polymerization reaction in major amounts of at least 95% by weight.

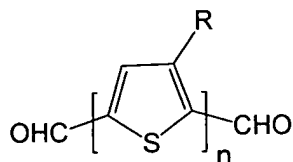
64 57  
87. The method of claim 80, wherein the polymer is formed from the polymerization reaction in major amounts of at least 99% by weight.

65 57  
88. The method of claim 80, wherein essentially all of a product from the polymerization reaction is the thiophene diol.

66 57  
89. The method of claim 80, wherein the introducing aldehyde groups to both ends of the chain of the intermediate polymer includes adding POCl<sub>3</sub> and N-methylformanilide to the intermediate polymer.

67  
90. The method of claim 80, wherein reducing the aldehyde groups comprises adding  $\text{LiAlH}_4$  to yield the poly-(3-substituted) thiophene diol.

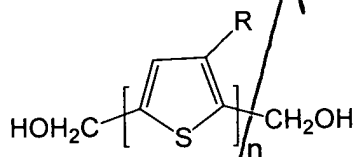
91. A thiophene polymer having aldehyde end groups, the polymer having the structure:



wherein R is a substituent selected from the group consisting of alkyl, polyether, and aryl, and n is greater than 1,

the polymer formed from the polythiophene polymer of claim 8.

92. A poly-(3-substituted) thiophene diol having the structure:



wherein R is a substituent selected from the group consisting of alkyl, polyether, and aryl, and n is greater than 1,

the diol formed from the polythiophene polymer of claim 8.

68  
93. A method of forming a diblock copolymer, comprising:  
combining a soluble thiophene monomer with an amide base and zinc chloride at a temperature ranging from  $-78^\circ\text{C}$  to  $-60^\circ\text{C}$ ;

adding an effective amount of a first  $\text{Ni(II)}$  catalyst to initiate a polymerization reaction and form an intermediate polymer;

adding a derivative compound represented by the formula  $\text{PFG-A-MX'}$  and a second  $\text{Ni(II)}$  catalyst to the intermediate polymer to form a protected thiophene polymer, wherein PFG is a protected hydroxyl or amine functional group, A is selected from the group consisting of alkyl and aromatic, M is selected from the group consisting of Zn or Mg, and X is a halogen; and

deprotecting the protected thiophene polymer in an acid environment to form a deprotected polymer having one functional end group;

adding an ATRP initiator and a base to the deprotected polymer to form a ATRP macroinitiator; and

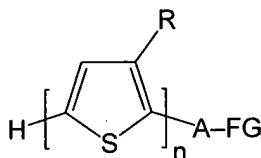
adding CuBr, at least one ATRP ligand, and at least one radically polymerizable monomer to the ATRP macroinitiator to form the diblock copolymer.

69  
94. The method of claim 93, wherein the ATRP initiator 2-bromopropionyl bromide.

110  
95. The method of claim 93, wherein the ATRP ligand is pentamethyldiethylenetriamine.

111  
96. The method of claim 93, wherein the radically polymerizable monomer is selected from the group consisting of styrenes, substituted styrenes, and acrylates.

112  
97. A method of forming a diblock copolymer, comprising:  
providing a deprotected polymer having one functional end group having the structure:



wherein R is selected from the group consisting of alkyl, polyether, and aryl; n is greater than 1; A is selected from the group consisting of alkyl and aromatic, and FG is a functional group selected from the group consisting of primary alkyl amine and primary alcohol;

(atom-transfer-radical-polymerization)

adding an ATRP initiator and a base to the deprotected polymer to form an ATRP macroinitiator; and

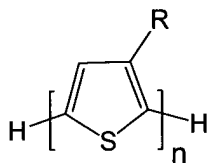
adding CuBr, at least one ATRP ligand, and at least one radically polymerizable monomer to the ATRP macroinitiator to form the diblock copolymer.

113  
98. The method of claim 97, wherein the ATRP initiator 2-bromopropionyl bromide.

114  
99. The method of claim 97, wherein the ATRP ligand is pentamethyldiethylenetriamine.

115  
100. The method of claim 97, wherein the radically polymerizable monomer is selected from the group consisting of styrenes, substituted styrenes, and acrylates.

116  
101. A method of forming a triblock copolymer, comprising combining a soluble thiophene with an organomagnesium reagent, wherein said organomagnesium reagent has the formula  $R'MgX'$  and  $R'$  is a substituent selected from the group consisting of alkyl, vinyl and phenyl and  $X'$  is a halogen, to form at least 90% by weight of a polythiophene intermediate polymer having the structure:



12340  
wherein R is a substituent selected from the group consisting of alkyl, polyether, and aryl, and n is greater than 1;

introducing aldehyde groups to both ends of a chain of the intermediate polymer;

reducing the aldehyde groups to yield a poly-(3-substituted) thiophene diol;

adding an ATRP <sup>(atom-transfer-radical-polymerization)</sup> initiator and a base to the diol to form a ATRP macroinitiator;

and

adding CuBr, at least one ATRP ligand, and at least one radically polymerizable monomer to the ATRP macroinitiator to form the triblock copolymer.

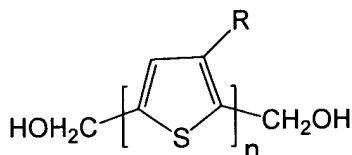
117  
102. The method of claim 101, wherein the ATRP initiator 2-bromopropionyl bromide.

118  
103. The method of claim 101, wherein the ATRP ligand is pentamethyldiethylenetriamine.

119  
104. The method of claim 101, wherein the radically polymerizable monomer is selected from the group consisting of styrenes, substituted styrenes, and acrylates.

80  
105.

A method of forming a triblock copolymer, comprising,  
providing a poly-(3-substituted) thiophene diol having the structure:



wherein R is a substituent selected from the group consisting of alkyl, polyether, and aryl, and n is greater than 1;

adding an ATRP <sup>atom-transfer radical polymerization</sup> initiator and a base to the diol to form a ATRP macroinitiator;

and

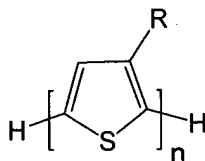
adding CuBr, at least one ATRP ligand, and at least one radically polymerizable monomer to the ATRP macroinitiator to form the triblock copolymer.

81  
106. The method of claim 105, wherein the ATRP initiator 2-bromopropionyl bromide.

82  
107. The method of claim 105, wherein the ATRP ligand is pentamethyldiethylenetriamine.

83  
108. The method of claim 105, wherein the radically polymerizable monomer is selected from the group consisting of styrenes, substituted styrenes, and acrylates.

84  
109. A method of forming a polyurethane copolymer, comprising  
combining a soluble thiophene with an organomagnesium reagent, wherein said organomagnesium reagent has the formula R'MgX' and R' is a substituent selected from the group consisting of alkyl, vinyl and phenyl and X' is a halogen, to form at least 90% by weight of a polythiophene intermediate polymer having the structure:

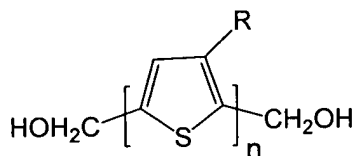


wherein R is a substituent selected from the group consisting of alkyl, polyether, and aryl, and n is greater than 1;



introducing aldehyde groups to both ends of a chain of the intermediate polymer;  
reducing the aldehyde groups to yield a poly-(3-substituted) thiophene diol;  
adding at least one dihydroxyl functional compound and at least one  
polyisocyanate to the diol to form the polyurethane copolymer.

85  
110. A method of forming a polyurethane copolymer, comprising,  
providing a poly-(3-substituted) thiophene diol having the structure:



wherein R is a substituent selected from the group consisting of alkyl, polyether, and  
aryl, and n is greater than 1;

adding at least one dihydroxyl functional compound and at least one  
polyisocyanate to the diol to form the polyurethane copolymer.

111. An intrinsically conductive copolymer, the copolymer having a conductivity  
ranging from  $10^{-8}$  S/cm to 150 S/cm.

112. The copolymer of claim 111, wherein the conductivity ranges from  $10^{-2}$  S/cm to  
150 S/cm.

113. The copolymer of claim 111, wherein the conductivity ranges from 1 S/cm to 150  
S/cm.

114. The copolymer of claim 111, wherein the conductivity ranges from 5 S/cm to 150  
S/cm.

115. The copolymer of claim 111, wherein the conductivity ranges from 10 S/cm to  
150 S/cm.

116. The copolymer of claim 111, wherein the copolymer is a diblock copolymer.

117. The copolymer of claim 111, wherein the copolymer is a triblock copolymer.

118. The copolymer of claim 111, wherein the copolymer is a polyurethane copolymer.

94  
119. An electrically conductive or optically sensitive polymeric material formed from the method of claim 93.

97  
120. An electrically conductive or optically sensitive polymeric material formed from the method of claim 97.

98  
121. An electrically conductive or optically sensitive polymeric material formed from the method of claim 101.

94  
122. An electrically conductive or optically sensitive polymeric material formed from the method of claim 105.

90  
123. An electrically conductive or optically sensitive polymeric material formed from the method of claim 109.

91  
124. An electrically conductive or optically sensitive polymeric material formed from the method of claim 110.

125. An electrically conductive or optically sensitive polymeric material comprising the copolymer of claim 111.